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Dynamics in complex and confined environments

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Abstract In 1929, Raman and Krishnamurti discovered small angle X-ray scattering (SAXS) Subsequently, SAXS developed into a powerful technique to study structure of soft matter, self-organized assemblies and biomolecules SAXS clearly shows hydration zones of organized assemblies in solution Most recently, several groups studied dynamics in the hydration layer of many molecular assemblies Recent studies indicate dynamics in many biological and self-organized molecular assemblies are vastly different from that in a simple liquid. Many ultrafast processes are dramatically slowed down in these environments. For instance, solvation dynamics which occur in a sub-picosecond time scale in bulk water exhibits a component in 100-1000 ps time scale In this article, we will discuss several examples of this phenomenon and the physical origin of the ultraslow dynamics

Keywords Complex systems, ultrafast laser spectroscopy

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Introduction

The discovery of Raman effect overshadowed a seminal contribution of Raman and Krishnamurti on scattering of X-ray by powdered crystal and amorphous materials. In 1929, Raman and Krishnamurti reported that finely powdered graphite exhibits appreciable scattering at a small angle [1]. This phenomenon known as small angle X-ray scattering (SAXS) arises from long range ordering over large interatomic distance (d), according to the Bragg equation $n\lambda = 2d \sin(\theta/2)$. Krishnamurthi applied this technique for the first time to study the structure of an amorphous substance, namely, amorphous carbon [2]. Because of the tremendous difficulty in separating the weak scattered radiation from the strong incident X-ray beam, it took nearly 40 years for this technique to be developed fully into an analytical tool for structure determination. With the development of synchrotron, this technique along with small angle neutron scattering (SANS) blossomed into the most powerful techniques to study structure of self-organized molecular assemblies in solution [3] The SAXS and SANS techniques provide detailed structural information on the hydration zones of a complex macromolecule or organized assembly in solution. The self-organized assemblies play a central role in many natural and biological processes and also in emerging technologies like fabricating nano-devices [4] and drug delivery [5]. Thus the discovery of SAXS by Raman and Krishnamurti may be considered as a fore runner to modern nanoscience. The most recent application of SAXS includes time-resolved study of structure of intermediates in protein folding and other structural transitions of biomolecules [6].

The hydration layer or more specifically, water molecules confined in an organized assembly control its structure, dynamics, biological function and molecular recognition. Structures of a few organized assemblies are shown in Figure 1. Most recently, several groups have applied NMR [7-8], ultrafast laser spectroscopy [9-11] and computer simulations [12-16] to study dynamics in these environments. In this article, we will give an overview of dynamics in these assemblies.

By far, the most interesting observation in dynamics in organized assemblies is the discovery of an ultraslow component of solvation dynamics of water. This component is 2-3 orders of magnitude slower than that in bulk water. There is a burgeoning interest to understand the physical origin of this component and its implications. According to the Nandi-Bagchi model, the biological water or the water molecules in the vicinity of a biological macromolecule consists of two kinds of water molecules- almost immobilized "bound" water molecules and "free" water molecules [17]. The slow relaxation arises as a result

of a dynamic equilibrium between them [17]. We will begin with study of fluorescence anisotropy decay which provides information on diffusion coefficient of fluorescent probes inside a confined environment. We will then discuss some recent results on solvation dynamics in many organized assemblies. Finally, we will give a brief outline of our current theoretical understanding of the slow dynamics in section 4.

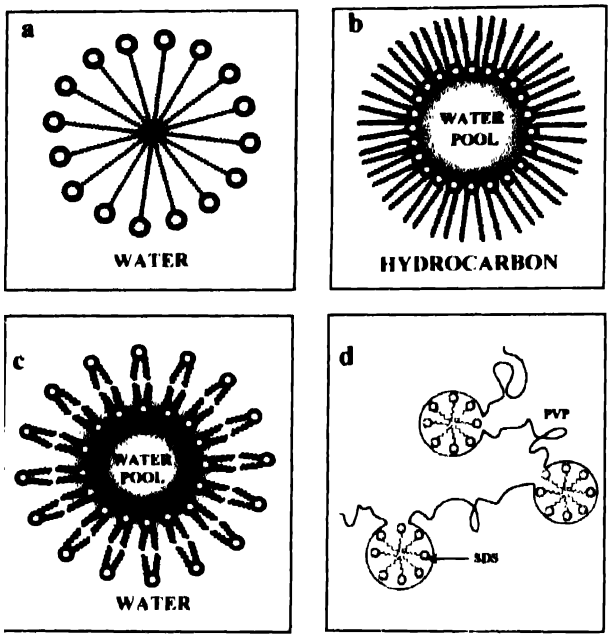


Figure 1. Structure of some organized assemblies. (a) micelle, (b) microemulsion, (c) lipid vesicles and (d) polymer surfactant aggregate

2. Fluorescence anisotropy decay

When a fluorescent probe is excited in a solution with a polarized light, a temporary anisotropy is created in the sample. At a short time, fluorescence intensity ($I_{\parallel}$) detected at a polarization parallel to the excitation is larger than the intensity ($I_{\perp}$) at perpendicular polarization. The time dependent fluorescence anisotropy $r(t)$ is defined as,

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2\, I_{\perp}(t)} \qquad (1)$$

In earlier studies, decay of $r(t)$ was used to estimate the microviscosity of a complex environment [18]. However, rotational dynamics of a probe in an organized assembly is complex and involves more than one kind of motion. According to the "wobbling-in-cone" model [19-21], fluorescence depolarization in a micelle arises as a result of three independent motions, (a) wobbling of the probe in a cone, (b) translational motion of the probe along the surface of the spherical micellar aggregates and (c) overall tumbling of the micelles. Because of the involvement of different kinds of motion, the decay of rotational function, $r(t)$ deviates from a single exponential decay. Recently, several authors have analyzed the biexponential decay of $r(t)$ and estimated the diffusion coefficients arising from different kind of motions [19-21]. From the detailed analysis of the decay of fluorescence anisotropy the coefficient for translational diffusion (D_t) of fluorescent probes in several organized assemblies have been determined [19-21]. D_t of organic molecules in micelles and polymer-surfactant aggregates are found to be about 5×10^{-10} m^2 s^{-1} which is very similar to that of an organic molecule in bulk water [22]. In summary, the translational diffusion of the probe in an organized assembly is not very different from that in a bulk water. This is in sharp contrast to the dramatic slowing down of solvation dynamics in organized assemblies.

3. 1 Solvation dynamics

Solvation dynamics refers to the dynamics of solute-solvent interaction i.e. how quickly the solvent dipoles rearrange around a solute dipole when it is created suddenly in a polar liquid. In this experiment, one uses a solute whose dipole moment is nearly zero in the ground state but is very large in the excited state. When such a solute molecule is in its ground state, the solvent dipoles remain randomly arranged (Figure 2). On excitation of the solute by an ultrashort light pulse, a dipole is created suddenly. Immediately after creation of the solute dipole, the solvent dipoles are randomly oriented and the energy of the system is high (Figure 2). With increase in time, as the solvent dipoles reorient the energy of the solute dipole decreases and its fluorescence maximum gradually shifts to lower energy i.e. towards longer wavelength. This is known as time dependent fluorescence Stokes shift (TDFSS). Evidently, at a short wavelength, the fluorescence corresponds to the unsolvated solute and exhibits a decay. At a long wavelength, the fluorescence originates from the solvated species and a rise precedes the decay. The rise at a long wavelength corresponds to the formation of the solvated species and hence, is a clear manifestation of solvation dynamics. Solvation dynamics is described by the decay of the time correlation function $C(t)$ which is defined as,

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \qquad (1)$$

where $\nu(0)$, $\nu(t)$ and $\nu(\infty)$ denote the observed emission energies (frequencies) at time zero, t and infinity, respectively

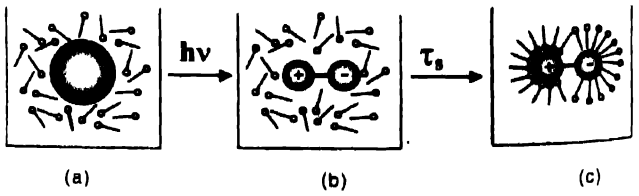


Figure 2. Solvation dynamics: arrangement of solvent dipoles (match sticks) (a) before excitation of the solute, (b) immediately after creation of the dipole by excitation of the solute and (c) fully solvated solute dipole

Obviously, $\nu(0) > \nu(t) > \nu(\infty)$. At $t = 0$, the value of $C(t)$ is one and at $t = \infty$ it is zero.

The continuum model predicts that the solvation time τ_s is $(\varepsilon_\infty / \varepsilon_0)\tau_D$, where ε_∞ and ε_0 are respectively, the high frequency and static dielectric constants of the solvent and τ_D, is the dielectric relaxation time. For water, τ_D is 8.3 ps [23] while ε_∞ and ε_0, are respectively, about 5 and 80. Thus the solvation time of water is 0.5 ps. Barbara *et al.* [24] observed that the solvation dynamics in water is biexponential with two components, 0.16 ps and 1.2 ps. Later, Fleming *et al.* [25] reported that solvation dynamics in water is described by a Gaussian component of frequency 38.5 ps^{-1} and a biexponential decay with components, 126 fs and 880 fs. Thus, solvation dynamics in bulk water occurs in < 1 ps time scale.

In a supramolecular assembly, a substantial fraction of the confined water molecules remains bound to the macromolecules by hydrogen bond and electrostatic attraction. We will now discuss several examples how confined water molecules cause a very long solvation time in 100-1000 ps time scale.

3.2 Solvation dynamics in supramolecular assemblies

(a) Micelles :

Micelles (Figure 1a) are spherical aggregates of surfactants formed in water and other polar solvents. According to SANS studies the structure of a micelle consists of an essentially "dry" hydrocarbon core and a polar peripheral shell [26-27]. The polar peripheral shell contains polar/ionic head groups, counter ions and the water molecules forming hydrogen bond bridges between the surfactant molecules. For the neutral surfactant, triton X-100 (TX) the hydration (palisade) layer is quite thick (20 Å). In the case of ionic micelles (cetyl trimethyl ammonium bromide, CTAB and sodium dodecyl sulfate, SDS) the hydration (Stern) layer is quite thin (6-9 Å) [26-27].

Solvation dynamics of the water molecules hydrogen bonded to the polar head groups of a micelle exhibit a very slow component in 100-1000 ps time scale [28]. The average solvation time in TX micelle has been found to be slower than that in SDS and CTAB micelles [28]. The difference in the solvation times has been ascribed to the structures of the micelles. In TX the thick hydration (palisade) layer completely shields the probe from bulk water. In the case of ionic micelles (CTAB and SDS), because of the thin hydration (Stern) layer, the probe remains partially exposed to bulk water and hence, displays fast dynamics.

The ultrafast components of solvation dynamics in a micelle are detected in a recent femtosecond upconversion study [29]. The solvation dynamics is found to be described by components of 2.1, 165 and 2050 ps for TX and 0.23, 6.5 (average 1.75 ps) and 350 ps for CTAB [29]. The ultrafast component of solvation dynamics is consistent with recent simulations on aqueous micelles [12,30].

The bile salt, sodium deoxycholate (NaDC) is a natural amphiphile which exhibits two critical micellar concentrations at ~ 10 mM (CMC1) and ~ 60 mM (CMC2). The structure of the bile salt micelle have been studied using SANS [31]. Above CMC1, bile salts form primary aggregates with the hydrophilic groups pointing outwards. Above CMC2, secondary aggregates are formed which resemble an elongated rod with a central hydrophilic core filled with water and the ions. The solvation dynamics of DCM in a secondary aggregate of NaDC is found to be triexponential with components of 110 ps, 700 ps and 2750 ps [32]. These components are significantly slower than those in bulk water.

(b) Reverse micelles and microemulsions :

In a non-polar solvent surfactant molecules aggregate to form a microemulsion, in which the water molecules exist as a nanometer sized droplet, called a "water pool." The water pool is surrounded by a layer of surfactant molecules whose polar head groups point inward (Figure 1b) [33-36]. The water pool in a microemulsion is an elegant model of confined water molecules. For the surfactant, AOT (sodium dioctyl sulfosuccinate) radius of the water pool is approximately $2w_0$ (Å) where w_0 denotes the water to surfactant molar ratio. In a water pool with $w_0 > 10$, solvation dynamics of water exhibits a component in 100-1000 ps time scale which is slower by three orders of magnitude compared to bulk water [9,37].

Apart from ordinary liquids at ambient pressure, microemulsions may also be created in a super-critical ($T > T_c$) or near-critical (T/T_c more than 0.75) fluid at a very high pressure. In a super-critical or near critical solvent one may vary the solvent density over a large range. Fulton *et al* studied the structure of a microemulsion of AOT in near-critical propane using small angle neutron scattering (SANS) [38]. They reported that in near-critical propane, for 125 mM AOT at a $w_0 = 15$, a well defined water pool is formed whose radius (≈ 20 Å) is independent of pressure in the range 2.4 – 47.4 MPa [38]. Solvation dynamics of C343 in AOT microemulsion has been studied in near-critical propane at 100 bar pressure and is found to be similar to that in an ordinary hydrocarbon at ambient pressure [39]. This shows that pressure does not affect the internal water pool but affects only the droplet-droplet interaction.

Addition of a polymer, poly-vinylpyrrolidone (PVP) to the water pool affects both the structure and dynamics in the water pool [40]. Effect of PVP on the structure of the water pool of an AOT microemulsion was studied by dynamic light scattering [40]. Hydrodynamic diameter of the microemulsion increases from 24 nm at 0 wt % PVP to 62 nm at 0.75 wt % PVP and then decreases to 31 nm at 2.5 wt % PVP [40]. The average solvation time is 350 ps in 0%, 115 ps in 0.75 wt % and 2500 ps in 2.5 wt % PVP.[25] It is proposed that in 0.75% PVP, solvation dynamics is fast because of the large size of the pool. For 2.5 wt % PVP, there

are 16 polymer particles of diameter 3.2 nm in each pool of diameter 31 nm and this makes the motion of the water molecules highly restricted in the pool [40].

(c) Lipids :

A lipid vesicle is an aqueous volume ("water pool") entirely enclosed by a membrane and dispersed in bulk water (Figure 1c) Thus a lipid vesicle is the closest model of a biological cell. Molecular dynamics simulations indicate that in a vesicle each surfactant molecule forms hydrogen bond to 4 5 water molecules and about 70% of the surfactant molecules are connected by hydrogen bond bridges [41] Solvent relaxation in lipids has been studied using time resolved fluorescence and NMR techniques [42-43] The solvation dynamics in lipid vesicles is found to be biexponential with one component of a few hundred ps and another of several thousand ps The slow solvation dynamics clearly demonstrates that the motion of the water molecules is highly constrained in the inner water pool of the vesicles.

(d) Polymer and polymer-surfactant aggregates .

A polymer-surfactant aggregate is a simple model system to study interaction between two complex systems and formation of new structures [44-45]. In a polymer-surfactant aggregate, the surface of the micelle remains shielded from bulk water by the polymer chains The structure of such an aggregate resembles a "necklace" with spherical micelles as beads and polymer chains as connecting threads (Figure 1d) In a polymer-surfactant aggregate the solvation dynamics is found to be appreciably slower than that in a micelle or in an aqueous solution of the polymer [46-47]. Solvation dynamics of TNS in PVP-SDS aggregate is described by two components, 300 ps and 2500 ps [46]. In contrast, solvation dynamics of TNS occurs in <50 ps in SDS micelles while in an aqueous solution of PVP the solvation dynamics is described by a major (85%) component of 60 ps. The slower solvation dynamics in PVP-SDS aggregate compared to the polymer PVP alone or SDS alone indicates severe restrictions on the mobility of the water molecule squeezed in between the polymer chains and the micellar (SDS) surface.

Castner et al. studied solvation dynamics in aqueous solution of an amphiphilic star-like macromolecule (ASM) which consists of a hydrophobic core and a peripheral hydrophilic shell [47]. The solvation dynamics in ASM is described by an ultrafast component of 0.95 ps (44%) and two very slow components of 361 ps (19%) and 3962 ps (37%).

(e) Proteins and DNA

Water molecules at the surface of a protein play a fundamental role in many binding processes (*e.g.* enzyme-substrate, antibody-antigen binding *etc*). In these interactions, the interacting surface has to be dehydrated before the ligand or the macromolecule binds to a protein. The high degree of specificity of the binding processes may arise as a result of the hydration layer of the proteins. Fleming et al. studied dynamics of a non-covalent probe, eosin in the hydration layer of a protein (lysozyme) using three photon echo peak shift [48]. They detected a very long component of 530 ps which is absent for free eosin in bulk water. This demonstrates that the water molecules in the immediate vicinity of the protein are highly constrained. Solvation dynamics of a non-covalent probe (DCM) in human serum albumin exhibits two components of 600 ps and 10000 ps [49]. Zewail et al. studied solvation dynamics of a probe bound non-covalently and covalently to a DNA binding protein (histone) [50]. They found that the dynamics is very fast and similar to bulk water [50]. They also studied solvation dynamics in a protein using tryptophan as the intrinsic probe. In bulk water solvation dynamics of tryptophan occurs in <1.1 ps [51]. However, in a single tryptophan protein, Subtilisin Carlsberg (SC) solvation dynamics of tryptophan exhibits a long component of 38 ps [51]. Interestingly, when a probe (dansyl) resides at a distance of 7.5 Å from the surface of the same protein (SC), the long component (38 ps) vanishes and the solvation dynamics resembles bulk water [51]. For another covalent probe buried about 5 Å below a protein surface, two components of 40 and 580 ps are reported [52]. Thus, solvation dynamics depends markedly on the distance of the water molecules from the protein surface.

Recently, solvation dynamics has been studied within the DNA double helix using a covalent probe. For this purpose Brauns *et al* attached a covalent probe to DNA in such a way that a coumarin probe replaces a base pair within the double helix [53]. They observed logarithmic relaxation from 40 ps to 40 ns [53]. The extremely slow dynamics has been ascribed to the presence of large number of conformational sub-states of DNA

(f) Nanoporous material: Hydrogel and Sol-gel Glass .

Optical Kerr effect studies on various liquids confined in a sol gel glass reveal a major bulk-like component and an additional component which is nearly 4 times slower [54]. In a sol-gel glass with 10 Å pores, the average solvation time of trapped water molecules is found to be 220 ps [55]. This is about 200 times slower than that in bulk water. The average solvation time of ethanol in bulk is 12.5 ps while it is 18.6 ps in a sol-gel glass with 75 Å pores and 35.9 ps in 50 Å pores [56]. In poly-acrylamide hydrogel with very big pores, the solvation dynamics is observed to be very fast (< 50 ps) [57].

4. Origin of the slow component of solvation dynamics

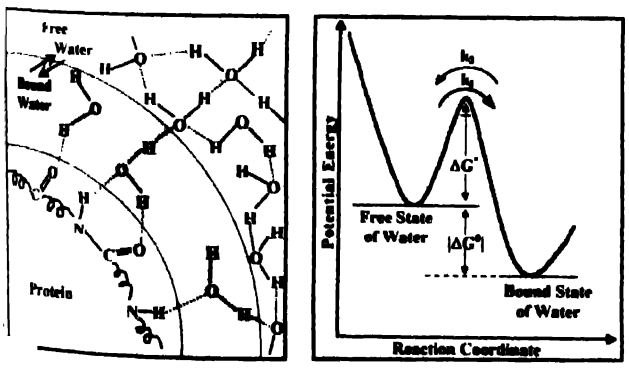
The very long component of the solvation dynamics in 1000 ps time scale may be explained semi-quantitatively as follows. For many organized assemblies, the dielectric relaxation time (τ_D) is about 10 ns while the dielectric constant (ε_0) of confined

/ater is close to that of alcohol (*i.e.* about 30). If we assume that ne high frequency dielectric constant (ε_∞) in a supramolecular ssembly is same as that in water, according to the continuum odel the solvation time is (5/30) × 10 ns or about 1600 ps.

An alternative source of the nanosecond (1000 ps) omponent may be as follows. It is possible that following xcitation by light when the probe solute becomes a large dipole t might migrate from a region of low polarity to another of high olarity. According to D_t of organic molecules in micelles and olymer-surfactant aggregates (about 5×10^{-10} m^2 s^{-1}) anslation may cause a displacement $(2D_t\tau)^{1/2} \approx 10$ Å per ns. Thus a displacement by 10Å may give rise to a nanosecond omponent.

The ultraslow component of solvation dynamics in organized assemblies may originate from the disruption of the hydrogen bond network of water. In the liquid phase, water molecules in close proximity mutually polarize each other. This results in an increase in the dipole moment of water from 1.85 D in the vapor to 2.6 D in the liquid phase. According to Berne *et al* the high binding energy and dielectric constant of liquid water arises because of the large contribution of the polarization effect [58] In an organized assembly, when the water molecule become bound to a macromolecule the polarization of a water molecule by the neighboring water molecules is prevented. This causes a marked decrease in the dielectric constant of water in a onfined environment.

According to Nandi and Bagchi, the slow dielectric relaxation results from a dynamic exchange between bound and free water [17] The magnitude of the slow component of solvation depends the free energy difference (ΔG^0) between bound and free water molecules (Figure 3) [17]. Nandi and Bagchi showed that he slow relaxation component varies from 35 ps (for ΔG^0 = 1 kcal mol^{-1}) to 2857 ps (for $\Delta G^0 = -4$ kcal mol^{-1}) [17].



igure 3. "Bound-free model" of-water in the biological systems

There have been many computer simulations on dynamics mplex assemblies. In one of the early simulations, Stillinger reported that a water molecule in the first solvation shell of drophobic solute is 20% slower than that in bulk [59]. The segmental motion of the polyethers was found to give rise to a 100 ps component of solvation dynamics [60]. A recent simulation on solvation dynamics indicates that at a liquid-liquid interface exhibits a slow component which is absent in bulk water or at the water-vapor interface [61].

Balasubramanian and Bagchi carried out a simulation of the hydrogen bond dynamics [12] and solvation dynamics [30] at the surface of a micelle. The most recent simulation suggests that the lifetime of the hydrogen bond between a water molecule and the polar head group of a micelle is about 13 times slower than that of a water-water hydrogen bond and the activation barrier for interconversion of free to bound water in a micelle is 3.5 kcal/mol [12].

For a microemulsion, Faeder and Ladanyi [13] carried out a simulation up to 10 ps and hence, did not detect the slow dynamics in 100-1000 ps time scale. Senapati and Chandra [14] showed that the dielectric constant and solvation time inside a microemulsion is lower than that in bulk water by less than one order of magnitude.

5. Conclusion

In recent years, time resolved X-ray scattering and ultrafast optical spectroscopic studies on self-organized assemblies coupled with computer simulations vastly improved our understanding of the structure and dynamics of these complex systems. The very high resolution both in length and time scale has revealed information with unprecedented precision. The new knowledge on the structure of the hydration zones of a biomolecule and the unusual dynamic features of the hydration layer have very serious biological implications. Solvation of the hydrophilic residues of a protein controls its structure while solvation of the polar transition state of a reaction facilitates the reaction. The fact that in the confined environment solvation dynamics is surprisingly slow is extremely relevant in electron transfer and other polar reactions occurring in biological assemblies. The ultimate goal of these studies is to explain site-specific chemistry at selected locations in a biological system. A comprehensive understanding of structural reorganizations of biomolecules e.g. protein folding or enzyme catalysis requires both knowledge of the structure and dynamics of the hydration layer.

In addition to structure and solvation dynamics, the hydrogen bond network of water plays a key role in many other phenomena, e.g. freezing [62]. The water molecules bound to some macromolecules do not freeze even at -300 A. Unfrozen water molecules help to sustain many organisms and plants at sub-zero temperatures. It should be noted that only very recently Ohmine et al. successfully simulated freezing of pure and unconfined water [62]. One of the future challenges would be simulation of the freezing of water in the hydration layer of a self-organized assembly.

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References

[1] C V Raman and P Krishnamurti *Nature* **124** 53 (1929)

[2] P Krishnamurti *Indian J. Phys.* **5** 473 (1930)

[3] B Chu and B S Hsiao *Chem. Rev.* **101** 1727 (2001)

[4] Y Xia, J Rodgers, K E Paul and G M Whitesides *Chem. Rev.* **99** 1823 (1999)

[5] A Muller and D F O'Brien *Chem. Rev.* **102** 727 (2002)

[6] S Doniach *Chem. Rev.* **101** 1763 (2001)

[7] G Otting, E Liepinsh and K Wuthrich *Science* **254** 974 (1991)

[8] V P Denisov, B H Jonsson and B Halle *Nature Struct. Biol.* **6** 253 (1999)

[9] N Nandi, K Bhattacharyya and B Bagchi *Chem. Rev.* **100** 2013 (2000)

[10] S K Pal, J Peon, B Bagchi and A H Zewail *J. Phys. Chem.* **B 106** 12376 (2002)

[11] K Bhattacharyya *Acc. Chem. Res.* (in press)

[12] S Balasubramanian, S Pal and B Bagchi *Phys. Rev. Lett.* **89** 115505-1 (2002)

[13] J Faeder and B M Ladanyi *J. Phys. Chem.* **B 105** 11148 (2001)

[14] S Senapathy and A Chandra *J. Phys. Chem.* **B 105** 5106 (2001)

[15] W M Gelbart and A. Ben-Shaul *J. Phys. Chem.* **100** 13169 (1996)

[16] R Allen, S Bandyopadhyay and M L Klein *Langmuir* **16** 10547 (2000)

[17] N Nandi and B Bagchi *J. Phys. Chem.* **B 101** 10954 (1997)

[18] J R Lakowicz *Principles of Fluorescence Spectroscopy*, (New York Plenum) (1999)

[19] E L Quitevis, A H Marcus and M D Fayer *J. Phys. Chem.* **97** 5762 (1993)

[20] N C Maiti, M M G Krishna, P J Britto and N Periasamy *J. Phys. Chem.* **B 101** 11051 (1997)

[21] S Sen, D Sukul, P Dutta and K Bhattacharyya *J. Phys. Chem.* **A 105** 7495 (2001)

[22] For instance, D_t of amino benzoic acid is 8×10^{-10} m^2/s ! *Handbook of Chemistry and Physics*, (Boca Raton, Fl : CRC) p 6 (1990)

[23] U Kaatze *Chem. Phys. Lett.* **203** 1 (1993)

[24] W Jarzeba, G C Walker, A E Johnson, M A Kahlow and P F Barbara *J. Phys. Chem.* **92** 7039 (1988)

[25] R Jimenez, G R Fleming, P V Kumar and M Maroncelli *Nature* **369** 471 (1994)

[26] S S Berr *J. Phys. Chem.* **91** 4760 (1987)

[27] S S Berr, E Caponetti, R R M Jones, J S Johnson and L J Magid *J. Phys. Chem.* **91** 5766 (1987)

[28] S K Pal, D Sukul, D Mandal, S Sen and K Bhattacharyya *Chem. Phys. Lett.* **327** 91 (2000)

[29] D Mandal, S Sen, T Tahara and K Bhattacharyya *Chem. Phys. Lett.* **359** 77 (2002)

[30] S Balasubramanian and B Bagchi *J. Phys. Chem.* **B 105** 12526 (2001)

[31] J Santhanlakshmi, G Shantha Lakshmi, V K Aswal, and P S Goya *Proc. Indian Acad. Sci. (Chem. Sci.)* **11** 355 (2001).

[32] S Sen, P Dutta, S Mukherjee and K Bhattacharyya *J. Phys. Chem.* **B 106** 7745 (2002)

[33] S P Moulik and B K Pal *Adv. Coll. Int. Sci.* **78** 99 (1998)

[34] A N Maitra *J. Phys. Chem.* **88** 5122 (1984)

[35] A Amrarene, M Gindre, J-Y Nicot, W Urbach and M Waks *J. Phys. Chem.* **B 101** 10751 (1997)

[36] D S Venables, K Huang and C A Schmuttenmaer *J. Phys. Chem.* **B 105** 9132 (2001)

[37] S K Pal, D Mandal, D Sukul and K Bhattacharyya *Chem. Phys. Lett.* **312** 178 (1999)

[38] E W Kaler, J F Billman, J L Fulton and R D Smith *J. Phys. Chem.* **95** 458 (1991)

[39] K Bhattacharyya, K Hara, N Kometani, Y Yozu and O Kajimoto *Chem. Phys. Lett.* **361** 136 (2002)

[40] S Sen, D Sukul, P Dutta and K Bhattacharyya *J. Phys. Chem. A* **106** 6017 (2002)

[41] M Pasenkiewicz-Gierula, V Takaoka, H Miyagawa, K Kitamura, and A Kusumi *J. Phys. Chem.* **A 101** 3677 (1997)

[42] J Sykora, P Kapusta, V Fidler and M Hof *Langmuir* **18** 571 (2002)

[43] S K Pal, D Sukul, D Mandal and K Bhattacharyya *J. Phys. Chem.* **B104** 4529 (2000)

[44] P G De Gennes *J. Phys. Chem.* **94** 8407 (1990)

[45] R Narenberg, J Kliger and D Horn *Angew. Chem. Int. Ed. Engl.* **38** 1626 (1999)

[46] S Sen, D Sukul, P Dutta and Bhattacharyya *J. Phys. Chem.* **B 106** 3763 (2002)

[47] L Frauchiger, H Shirota, K E Uhrich and E W Castner (Jr) *J. Phys. Chem.* **B 106** 7463 (2002)

[48] X J Jordandies, M J Lang, X Song and G R Fleming *J. Phys. Chem.* **B103** 7995 (1999)

[49] S K Pal, D Mandal, D Sukul, S Sen and K Bhattacharyya *J. Phys. Chem.* **B 105** 1438 (2001)

[50] D Zhong, S K Pal and A H Zewail *Chemphyschem* **2** 219 (2001)

[51] S K Pal, J Peon and A H Zewail *Proc. Natl. Acad. Sci. (USA)* **99** 1763 (2002)

[52] D Mandal, S Sen, D Sukul, K Bhattacharyya, A K Mandal, R Banerjee and S Roy *J. Phys. Chem.* **B 106** 10741 (2002)

[53] E B Brauns, M L Madaras, R S Coleman, C J Murphy and M A Berg *Phys. Rev. Lett.* **88** 158101-1 (2002)

[54] B J Loughnane, R A Farrer, A Scodinu, T Reilly and J T Fourkas *J. Phys. Chem.* **B 104** 5421 (2000)

[55] S K Pal, D Sukul, D Mandal, S Sen and K Bhattacharyya *J. Phys. Chem.* **B 104** 2613 (2000)

[56] R Bauman, C Ferrante, F W Deeg and C Brauchle *J. Chem. Phys.* **114** 5781 (2001)

[57] A Datta, S Das, D Mandal, S K Pal and K Bhattacharyya *Langmuir* **13** 6922 (1997)

[58] S W Rick, S J Stuart and B J Berne *J Chem Phys.* **101** 6141 (1994)

[59] A Geiger, A Rahman and H Stillinger *J Chem. Phys* **70** 263 (1979)

[60] R Olander and Nitzan *J. Chem Phys* **102** 7180 (1995)

[61] D Michael and I Benjamin *J Chem Phys* **114** 2817 (2001)

[62] I Ohmine, M Matsumoto and S Saito *Nature* **416** 409 (2002)

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